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Liquid crystalline polymers containing mesogenic units based on half-disc and rod-like moieties

2. Synthesis and characterization of poly{2-[3,4,5-tri[*p*-(*n*-dodecan-1-yloxy)benzyloxy]benzoate]-7-[*p*-11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane}*

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INTRODUCTION

Mesogenic units based on various combinations of half-disc and rod-like moieties represent a novel class of liquid crystals. Combinations of two half-disc and a rod-like moieties lead to phasmidic liquid crystals which display either phasmidic i.e., columnar oblique (Φ_{ob}) and hexagonal (Φ_h), [1-6] or biaxial nematic (N_b)[7] mesophases. Alternatively, half phasmids, or combinations of a half-disc and a rod-like moiety provide the most succesfull architectural approach to the synthesis of liquid crystals displaying N_b mesophases.[2,6,8]

The first examples of liquid crystal polymers containing phasmidic and half phasmidic mesogens were reported from our[9] and from Ringsdorf's[10] laboratories.

Both low molar mass and polymer liquid crytstals containing phasmidic or half phasmidic mesogens synthesized so far, contain a rod-like or cone-like moiety connected to the half disc part of the mesogen.[1-6]

The goal of this paper is to present the synthesis of the first example of liquid crystalline polymer based on a half-disc and a kinked-rigid moiety, i.e., poly{2-[3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate]-7-{p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane}.

EXPERIMENTAL

Materials

All materials were of commercial source and were used as received or were purified by conventional techniques.

Techniques

The techniques used in the characterization of intermediary derivatives and of polymers (200 MHz ^{1}H-NMR, IR, DSC, GPC, HPLC and thermal optical polarized microscopy) were described elsewhere.[11,12]

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*Part 1: V. Percec and J. Heck: J. Polym. Sci. Polym. Lett., submitted

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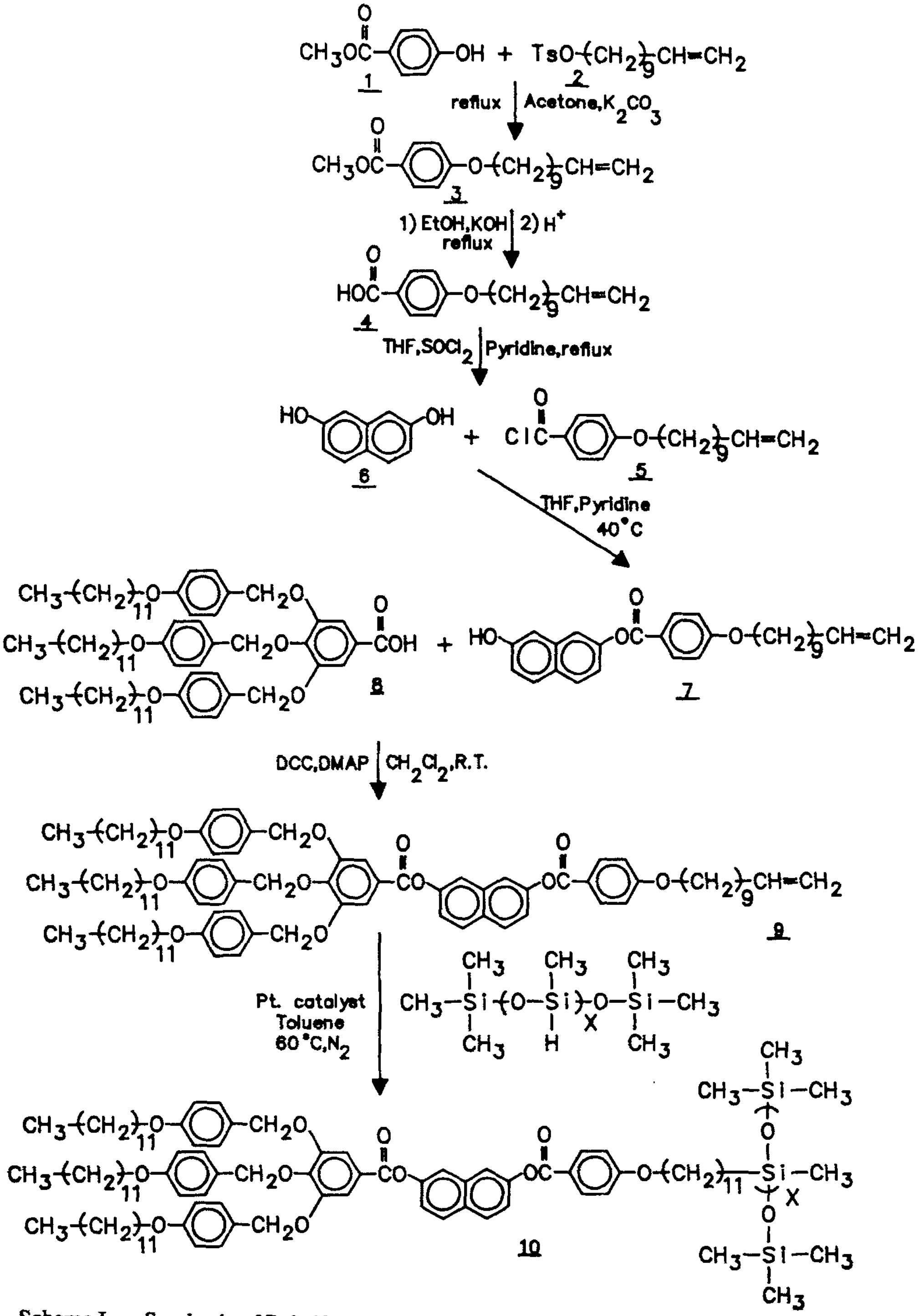

Scheme I: Synthesis of Poly{2-[3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane} (10)

Monomers and Polymers

Scheme I outlines the synthesis of monomers and polymers.

p-(10-Undecen-1-yloxy)benzoic Acid (4)

A mixture containing 16.57g (0.051 mol) of 10-undecen-1-yl tosylate,[9] 7.90g (0.052 mol) methyl-4-hydroxybenzoate, 30g (0.2 mol) anhydrous K_2CO_3 and 250 ml acetone was heated at reflux temperature for 16 hr. After cooling to room temperature, the reaction mixture was poured into water, methylene chloride was added, and the mixture was acidified with formic acid. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated. The resulting solid was first purified by column chromatography (basic alumina, methylene chloride eluent), then it was mixed with 200 ml 1N KOH solution in ethanol and heated to reflux temperature for 2 hr. After cooling to room temperature, the reaction mixture was acidified with HCl. Water was added until a precipitate formed. The precipitate was filtered, washed with water and recrystallized from methanol/water to yield 9.45g (63%) of white crystals. Purity: 89% (HPLC). mp, 81°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.31 (m, 12 H, $-(C\underline{H}_2)-$), 1.81 (m, 2H, $-C\underline{H}_2-CH_2-O-Ph$), 2.03 (m, 2H, $-C\underline{H}_2-CH=CH_2$), 4.02 (t, 2H, $-C\underline{H}_2-O-Ph$), 4.93 (d, 1H, $C\underline{H}_2=CH-CH_2-$ trans), 5.00 (d, 1H, $C\underline{H}_2=CH-CH_2-$ cis), 5.80 (m, 1H, $-C\underline{H}=CH_2$), 6.95 (d, 2H, -O-Ph-$\underline{H}$-COOH ortho from -O-), 8.03 (d, 2H, -O-Ph-$\underline{H}$-COOH ortho from -COO-). IR (KBr plate): 1670 cm^{-1} (ν-C=O).

2-Hydroxy-7-[p-(10-undecen-1-yloxy)benzoate]Naphthalene (7)

To a mixture containing 3.6g (0.012 mol) of 4 dissolved in 300 ml of dry THF were added 3 ml (0.037 mol) of dry pyridine and 1 ml (0.014 mol) of thionyl chloride, and the reaction mixture was refluxed for 15 min. After cooling to 0°C, 10g (0.06 mol) of 2,7-dihydroxynaphthalene was added and the reaction mixture was stirred at 40°C for 10 hr. After cooling to room temperature, water and chloroform were added to the reaction mixture. The chloroform layer was separated, dried over anhydrous $MgSO_4$, filtered and the solvent was distilled in a rotavapor. The resulting solid was passed through a chromatographic column (silica gel, chloroform eluent) and the concentrated chloroform solution was precipitated into hexane. The precipitate was stirred for 18 hr at room temperature and then was filtered and dried to yield 2.99g (54%) of a white solid. Purity: 99% (HPLC). mp, 138°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.33 (m, 12H, $-(C\underline{H}_2)-$), 1.80 (m, 2H, $-C\underline{H}_2-CH_2-O-Ph$), 2.00 (m, 2H, $C\underline{H}_2-CH=CH_2$), 4.02 (t, 2H, $-C\underline{H}_2-O-Ph$), 4.93 (2 overlapped d, 2H, $-CH=C\underline{H}_2$), 5.30 (b, 1H, -O$\underline{H}$), 5.78 (m, 1H, $C\underline{H}=CH_2$), 6.97 (m, 4H, -COO-Nf-$\underline{H}$-OH 6 and 8 positions, and -O-$\underline{H}$-PhCOOH ortho from -O-), 7.17 (d, 1H, -COONf-$\underline{H}$-OH 3 position), 7.47 (s, 1H, -COONf-$\underline{H}$-OH 1 position), 7.70-7.81 (2 overlapped d, -COONf-H-OH 4 and 5 positions), 8.18 (d, 2H, -O-PhH-COO- ortho from -COO-). IR (KBr plate): 1705 cm^{-1} (ν-C=O), 3410 cm^{-1} (ν-OH).

2-{3,4,5-Tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate}-7-[p-(10-undecen-1-yloxy)benzoate]naphthalene (9)

A solution containing 0.41g (0.4 mmol) of 8,[9] 0.23g (0.5 mmol) 7, 0.10g (1.2 mmol) of dicyclohexylcarbodiimide and 0.15g (1.2 mmol) of 4-dimethylaminopyridine in 15 ml of dry methylene chloride was stirred for 6 hr at room temperature. The resulting precipitate was filtered and the methylene chloride solution was precipitated into methanol/water (20/1). The resulting precipitate was filtered and recrystallized from a mixture of diethyl ether/methanol. The final purification was performed by column chromatography (basic alumina, methylene chloride eluent) to yield 0.39g (68%) of white crystals. Purity: 99% (HPLC). mp, 98.1°C (DSC, 20°C/min). ^{1}H-NMR (CDCl$_3$, TMS, δ, ppm): 0.84 (t, 9H, -CH$_3$), 1.26 (m, 66H, -(CH$_2$)-), 1.74 (m, 8H, -CH$_2$-CH$_2$-O-Ph), 1.99 (m, 2H, -CH$_2$-CH=CH$_2$), 3.93 (m, 6H, -CH$_2$-OPh-CH$_2$O-), 4.02 (t, 2H, CH$_2$-CH$_2$-OPh-COO), 4.92 (2 overlapped d, 2H, -CH=CH$_2$), 5.03 (s, 2H, -OPhCH$_2$OPh-COO- from para position), 5.06 (s, 4H, -OPhCH$_2$O-Ph-COOH from 3 and 5 positions), 5.75 (m, 1H, -CH=CH$_2$), 6.77 (d, 2H, -OHPhCH$_2$-OPhCOO- ortho from -O- of internal benzylic unit), 6.80 (d, 4H, -OH-Ph-CH$_2$-OPhCOO- ortho from -O- of external benzylic units), 6.98 (d, 2H, -CH$_2$-CH$_2$-O-PhHCOO- ortho from -O-), 7.27 (d, 4H, -O-PhHCH$_2$O-PhCOO- ortho from -CH$_2$- of internal benzylic unit and 3 and 6 protons of Nf), 7.35 (d, 4H, -O-PhH-CH$_2$OPhCOO- ortho from -O- of external benzylic units), 7.54 (s, 2H, -Ph-CH$_2$OPhHCOO-), 7.64 (2 overlapped d, 2H, 1 and 8 protons of Nf), 7.94 (d, 2H, 4 and 5 protons of Nf), 8.29 (d, 2H, -CH$_2$-CH$_2$O-PhHCOO- ortho from -COO-). IR (KBr plate): 1730 cm^{-1} (ν-C=O).

Poly{2-[3,4,5-tri[p-dodecan-1-yloxy)benzoate]-7-[p-(11-undecan-1-yloxy)benzoate]naphthalene]methyl siloxane} (10)

To a flame-dried 5 ml test tube containing a microstirring bar were added 0.50g (0.35 mmol) 9, 0.0210g (0.35 mmol) poly(hydrogenmethylsiloxane) (Mn=1500 from Petrarch), 2 ml dry toluene and 3 drops (about 0.06g) of platinum divinyltetramethyldisiloxane complex (solution in xylene from Petrarch). The reaction mixture was purged with nitrogen and the tube was sealed with a cork stopper covered with teflon tape. The reaction mixture was heated for 24 hr at 60°C, cooled and precipitated into methanol. The precipitated was filtered, dissolved in THF and precipitated in acetone (by the technique described in the previous publication[9]) to yield 0.26g (52%) of white solid. Purity: 99% (HPLC). Mn=37000, Mw/Mn=1.7 (GPC with polystyrene standards).

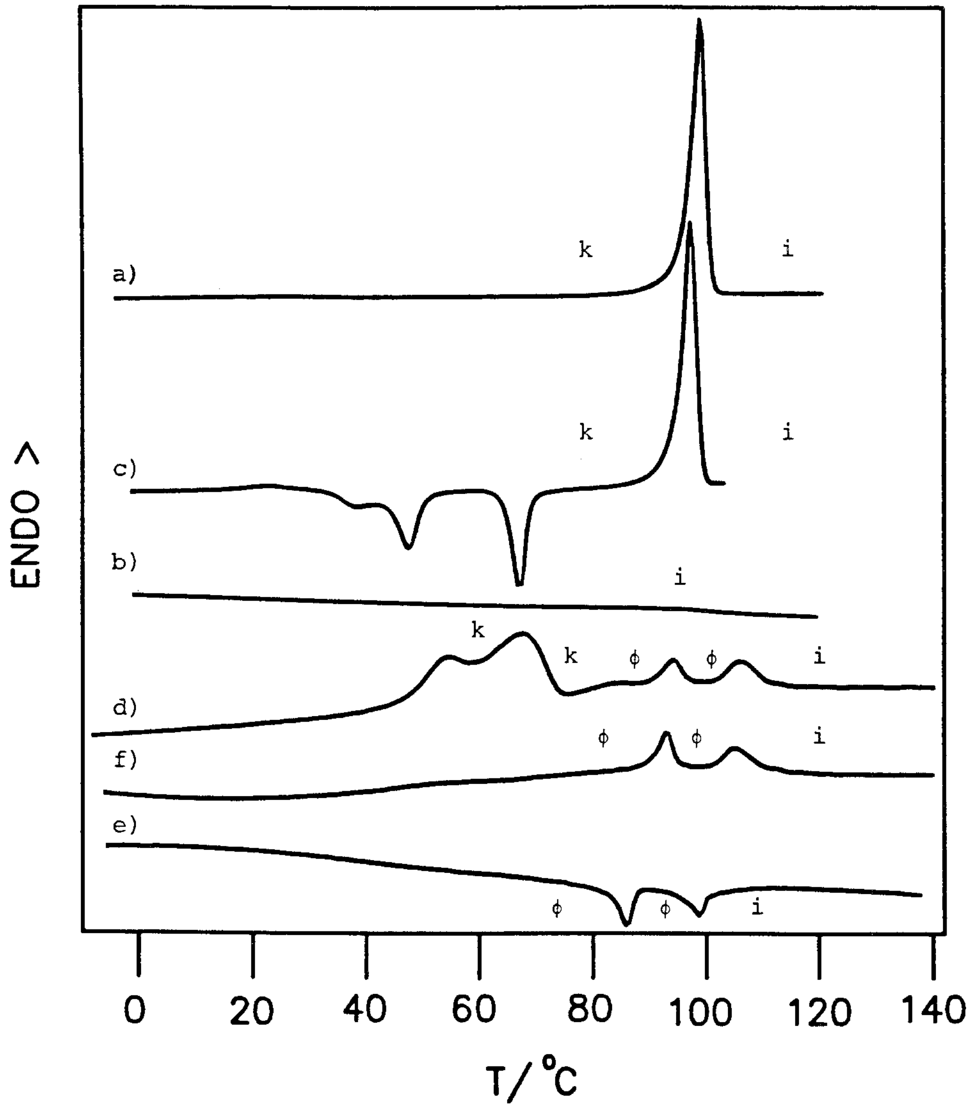

Figure 1: Heating and cooling DSC (20°C/min) traces of : 9 (a, first heating scan; b, cooling scan; c, second heating scan) and 10 (d, first heating scan; e, cooling scan; f, second heating scan)

Table I Thermal characterization of 9 and 10 (g=glassy phase, k=crystalline phase, Φ=phasmidic mesophase)

Sample no.	GPC		phase transitions(^{o}C) and corresponding enthalpy changes(kcal/mru)	
	M_n	M_w/M_n	heating	cooling
9	---	---	k 98(26.3) i g 17 k 34,44(-12.0)^{ab} k 64(-8.8)^{b} k 94(25.1) i	i 10 g
10	37000	1.7	k 53,67(5.6)^{a} k 82(0.06) Φ 93(0.4) Φ 104(0.6) i g 44 Φ 92(0.6) Φ 104(0.6)	i 99(0.6) Φ 87(0.6) Φ

[a] combined enthalpy for overlapped transitions

[b] crytallization during heating

RESULTS AND DISCUSSION

Synthesis of 9 and 10 are outlined in Scheme I. 8 was prepared as reported in the previous publication from this series.[9] Some representative DSC traces of 9 and 10 are presented in Figure 1. Table I summarizes the thermal transition temperatures and the corresponding enthalpy changes of 9 and 10. 9 melts at 98°C directly into an isotropic liquid. On cooling it does not crystallize. However, it crystallizes on the subsequent heating scan. 10 exhibits three melting endotherms at 53, 67 and 82°C, followed by two enantiotropic mesophases. The first mesophase changes at 93°C into a second mesophase which undergoes isotropization at 104°C. On subsequent heating and cooling scans, 10 exhibits only the two enantiotropic mesophases. The degree of supercooling of the phase transitions associated with these two mesophases on the cooling scan is very low. Both mesophases were characterized by thermal optical polarized microscopy. Figure 2 shows a characteristic texture displayed by 10 after annealing for 8 hr at 103°C. It exhibits a fan-shaped texture which is characteristic for Φ_{ob} and Φ_h mesophases.[1] Upon cooling below 87°C, a small change in this texture is observed. However, the texture remains fan-shape type. We can assume that 10 displays one or even two phasmidic mesophases. The discrimination between Φ_{ob} and Φ_h mesophases requires X-ray scattering experiments. Research on this line is in progress.

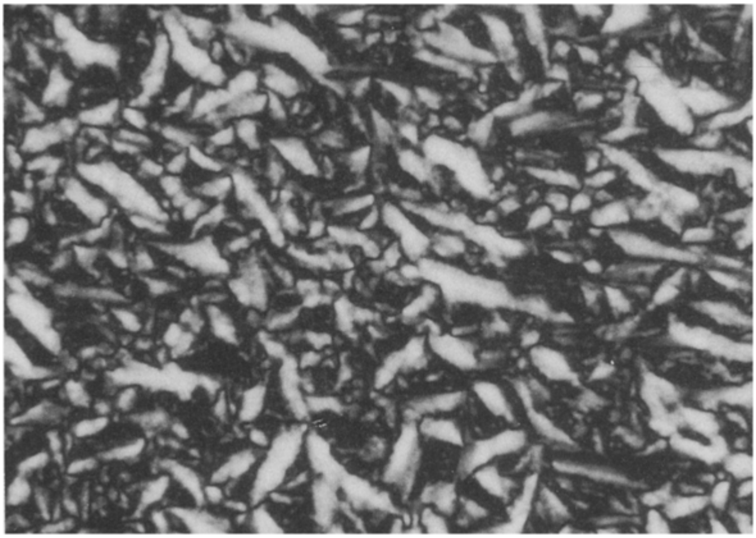

Figure 2: Representative optical polarized micrograph (100x) of fan-shaped texture of 10 after 8 hr annealing at 103°C

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REFERENCES

1. J. Malthete, A. M. Levelut and N. H. Tinh, J. Phys. Lett., 46, L-875(1985)
2. J. Malthete, L. Liebert, A. M. Levelut and Y. Galerne, C. R. Acad. Sci. Paris, 303, Series II, 1073(1986)
3. J. Malthete, N. H. Tinh and A. M. Levelut, J. Chem. Soc., Chem. Commun., 1986, 1548
4. A. M. Levelut, J. Malthete, C. Destrade and N. H. Tinh, Liq. Cryst., 2, 877 (1987)
5. D. Guillon, A. Skoulios and J. Malthete, Europhys. Lett., 3, 67(1987)
6. J. Malthete, A. Collet and A. M. Levelut, Liq. Cryst., 5, 123(1989)
7. K. Praefcke, B. Kohne, B. Gundogan, D. Demus, S. Diele and G. Pelzl, Mol. Cryst. Liq. Cryst., Lett., 7, 27(1990)
8. S. Chandrasekhar, B. R. Ratna, B. K. Sadashiva and V. N. Raja, Mol. Cryst. Liq. Cryst., 165, 123(1988)
9. V. Percec and J. Heck, Am. Chem. Soc. Polym. Chem. Div. Polym. Prepr., 30(2), 450(1989); V. Percec and J. Heck, J. Polym. Sci. Polym. Lett. Ed., submitted
10. C. Liu, H. Ringsdorf M. Ebert, R. Kleppinger and J. H. Wendorff, Liq. Cryst., 5, 1841(1989)
11. V. Percec and B. Hahn, Macromolecules, 22, 1588(1989)
12. V. Percec and R. Rodenhouse, Macromolecules, 22, 4408(1989)

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